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The Crystal and Molecular Structure of 8, 8-Dicyanoheptafulvene

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Crystals of 8, 8-dicyanoheptafulvene, $C_{10}H_6N_2$, are monoclinic, with two molecules in a unit cell with the dimensions $a=7.84$, $b=13.14$, $c=3.99$ Å, and $\beta=97.9°$; the space group is $P2_1/m$. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs and measured visually against a standard scale. A trial structure was constructed from the Patterson projections, $P(u, v)$ and $P(u, w)$, and a Harker section, $P(u, 1/2, w)$. The atomic coordinates and anisotropic temperature factors were refined by the least-squares method. The final R factor for (hkl) reflections is 0.107. A considerable bond alternation in the conjugated seven-membered ring has been observed. The average long and short bond lengths in the ring are 1.44 and 1.34 Å respectively. The shortest C=C bond measures 1.31 Å, which is shorter than that in ethylene. The exocyclic C=C bond length is 1.42 Å, suggesting a considerable dipolar resonance structure, one which may be responsible for the stability of the compound. The C≡N bond length is 1.13 Å. The molecule deviates slightly from being planar; it lies nearly parallel to the (101) plane. All the intermolecular separations correspond to normal van der Waals interactions; the perpendicular distance between the molecular planes is 3.4 Å. The thermal motion was interpreted in terms of rigid body vibrations, and the bond lengths and angles were corrected for the rotational oscillations.

Recently 8, 8-dicyanoheptafulvene $C_{10}H_6N_2$ (I), a derivative of the non-alternant hydrocarbon

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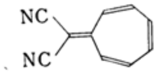
heptafulvene, has been synthesized in several laboratories.[1-3]



I

While heptafulvene itself decomposes at room temperature and cannot be isolated,[4] this derivative is very stable at temperatures up to 300°C, and reacts neither with dienophiles nor with electrophilic reagents. It will be interesting to ascertain the structural basis of this high stability. The present work has been underatken out of our general concern with the molecular geometry of aromatic seven-membered ring compounds, which should give fundamental information for investigating quantitatively the physical and chemical properties of such systems.

A preliminary report on the structure has already been published.[5]

Experimental

8, 8-Dicyanoheptafulvene (I) was prepared by the method given by Kitahara and Doi (1959).[6] It crystallizes from a methanol solution in the form of red needles elongated along the c axis.

The crystallographic and physical data obtained are: 8, 8-Dicyanoheptafulvene $C_{10}H_6N_2$, m. p. 199—200°C; Monoclinic, $a=7.84$ Å, $b=13.14$ Å, $c=3.99$ Å, and $\beta=97.9°$. Absent spectra, ($0k0$) when k is odd. Space group, $P2_1$ or $P2_1/m$. Two molecules per unit cell. Volume of the unit cell; 407.1 Å.^{3} Density (by flotation); 1.27_2 g. cm^{-3}. Density (calculated); 1.26_4 g. cm^{-3}. Linear absorption coefficient for Cu$K\alpha$ radiation; $\mu=6.31$ cm^{-1}. Total number of electrons per unit cell; $F(000)=160$.

Equi-inclination Weissenberg photographs for 0—3 layers were taken around the c axis, using Cu$K\alpha$ radiartion at room temperature. Precession photographs for ($h0l$) zone were also taken, using Cu$K\alpha$ and Mo$K\alpha$ radiations, in order to determine the relative scales among the layers. The crystal used was square in cross-section, with rectangular dimensions: 0.02×0.01 cm.

Intensities were estimated by visual comparison with a standard scale prepared with the same crystal. The multiple-film technique was applied to correlate strong and weak reflections, ranging in relative intensity from 10000 to 1. Reflections from 514 planes were observed out of 930 accessible (hkl)'s. The corrections for Lorentz and polarization factors were made in the usual way, while that for absorption was omitted. Tentative scale and temperature factors were obtained by Wilson statistics,[7] the latter being $B=2.0$ Å^2.

Structure Determination

The sharpened Patterson projection, $P(u, v)$, shown in Fig. 1, was calculated with the relative intensities of 100 observed ($hk0$) reflections. A planar molecular model was set up by assuming plausible bond distances and angles, the hydrogen atoms being ignored. The molecular orientation was obtained by seeking the best fit of the intramolecular vector sets with the Patterson function. The long axis of the molecule is perpendicular to the b axis, and the molecule lies nearly parallel to the (101) plane. Vector sets at the best fit are indicated by the spots in Fig. 1. This orientation was also supported by another Patterson projection, $P(u, w)$, shown in Fig. 2.

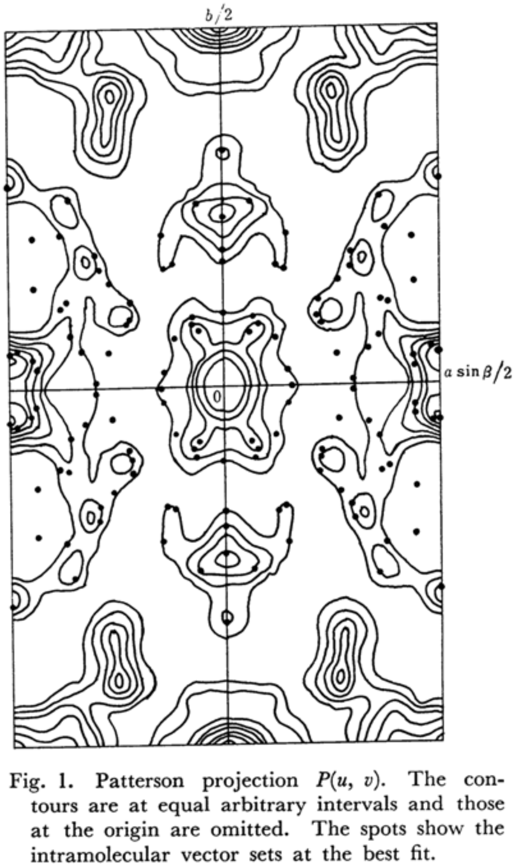


Fig. 1. Patterson projection $P(u, v)$. The contours are at equal arbitrary intervals and those at the origin are omitted. The spots show the intramolecular vector sets at the best fit.

If the space group is $P2_1$, the y coordinate of an atom can be arbitrarily chosen. Therefore, approximate y coordinates of the other atoms were

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1) T. Nozoe, T. Mukai, K. Osaka and N. Shishido, This Bulletin, **34**, 1384 (1961).

2) K. Hafner, H. W. Riedel and M. Danielisz, *Angew. Chem.*, **75**, 344 (1963); *Angew. Chem. internat. Edit.*, **2**, 215 (1963).

3) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964).

4) W. v. E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

5) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara, This Bulletin, **38**, 1230 (1965).

6) Y. Kitahara and K. Doi, ibid., to be published.

7) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

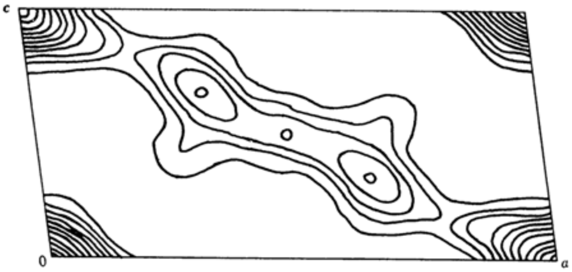

Fig. 2. Patterson projection $P(u, w)$. The contours are at equal arbitrary intervals.

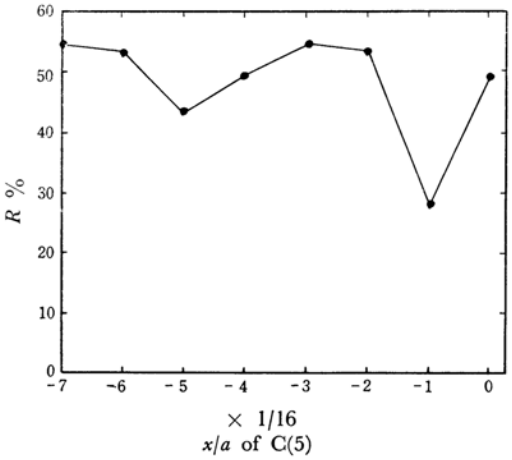

Fig. 3. One dimensional R map computed with all ($hk0$) reflections.

given by the model. The x coordinates were obtained by a one-dimensional minimum residual calculation,[8] where the discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was computed for all ($hk0$) reflections. Figure 3 shows the variation of R against the x coordinate of the reference atom, C(5). The first electron density projection, $\rho(x, y)$, was computed with phases based on these parameters. It clearly showed a definite molecular shape, without any ghost peaks. The atomic coordinates read off from the Fourier synthesis were refined by the block-diagonal matrix least-squares method. After five cycles of the refinement, the R factor reached 0.078 for the observed reflections. The atomic arrangement in the unit cell thus obtained suggested the existence of a mirror plane perpendicular to the b axis, within the limits of error. Moreover, the pyroelectricity test and the statistical investigation of the intensity data,[9] $|F_o(hk0)|^2$'s and $|F_o(hk1)|^2$'s respectively, showed that the crystal should be centrosymmetrical. Therefore, the space group of this crystal was chosen to be $P2_1/m$ for the subsequent studies.

In order to obtain the z coordinates, a sharpened Harker section, $P(u, 1/2, w)$, was calculated, as is shown in Fig. 4. There were two rows of peaks parallel to the (101) plane. The high peaks near the c axis were interpreted as follows. If the y coordinates of the two atoms are euqal, the non-Harker peak due to these atoms should be placed at the midpoint of their Harker peaks and be doubly weighted.[10] In the tentative structure of 8, 8-dicyanoheptafulvene, there were three pairs of atoms at the same y level; i. e., C(4) and C(5), C(1) and C(6), and C(1′) and C(6′), their corresponding Harker peaks being indicated by the spots in Fig. 4. The non-Harker peaks due to these atoms pairs were situated at nearly the same position and gave the considerably high peaks mentioned above.

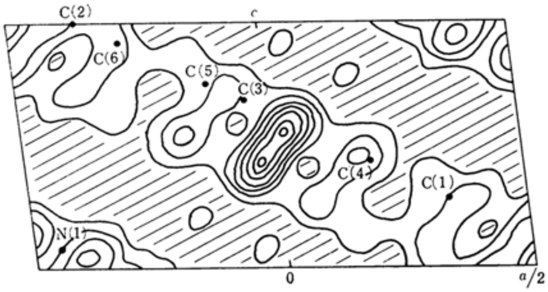

Fig. 4. Harker section $P(u, 1/2, w)$. The contours are at equal arbitrary intervals. The region lower than the starting contour is indicated by oblique lines. The spot shows the position of the expected Harker peak of each atom.

The coordinates thus obtained were then refined by the block-diagonal matrix least-squares method with anisotropic temperature factors, all (hkl) reflections being used. The parameters of the hydrogen atoms were also refined; they were first located at a distance of 1.0 Å outward radially

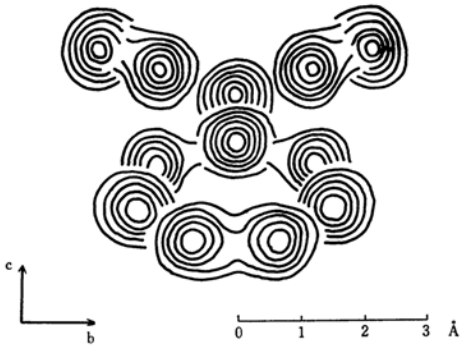

Fig. 5. Composite electron density diagram of sections parallel to (100). The contours are at intervals of 1.0 e.Å^{-3} starting with 2.0 e.Å^{-3}.

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[8] A. K. Bhuiya and E. Stanley, *Acta Cryst.*, **17**, 746 (1964).

[9] E. R. Howells, D. C. Phillips and D. Rogers, ibid., **3**, 210 (1950).

[10] G. Albrecht and R. B. Corey, *J. Am. Chem. Soc.*, **61**, 1087 (1939).

TABLE I. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	10FO	10FC
K,L=	0,	0
1	202	177
2	212	-196
3	316	-292
4	126	-109
5	19	8
6	42	46
7	23	28
8	51	-49
9	16	9
K,L=	1,	0
1	152	-137
2	244	233
3	110	-88
4	14	12
5	0	-2
6	67	60
7	35	-29
8	16	13
9	25	21
K,L=	2,	0
0	370	-408
1	69	-55
2	251	-229
3	92	76
4	88	82
5	61	51
6	23	22
7	20	-29
8	25	17
9	0	-2
K,L=	3,	0
1	109	108
2	103	105
3	31	-22
4	183	-178
5	56	43
6	0	7
7	29	-18
8	30	-24
9	0	-1
K,L=	4,	0
0	288	-305
1	15	4
2	326	309
3	103	91
4	31	30
5	37	-40
6	109	-101
7	31	-29
8	0	7
9	0	8
K,L=	5,	0
1	145	135
2	55	-47
3	97	-90
4	0	2
5	13	14
6	57	58
7	55	49
8	0	-0
9	22	-22
K,L=	6,	0
0	0	-8
1	82	-74
2	10	6
3	75	-60
4	85	-79
5	0	3
6	78	70
7	65	67
8	0	6
K,L=	7,	0
1	28	-21
2	19	4
3	26	18
4	68	66
5	55	-47
6	48	-52
7	19	-22
8	0	0
K,L=	8,	0
0	49	50
1	78	71
2	0	-11
3	73	65
4	19	-24
5	57	-54
6	0	10
7	15	-13
8	0	-7
K,L=	9,	0
1	103	-100
2	26	-24
3	78	74
4	0	0
5	37	32
6	16	-19
7	0	-4
8	18	17
K,L=	10,	0
0	90	-84
1	93	-89
2	0	7
3	14	19
4	66	62
5	26	25
6	30	-31
K,L=	11,	0
1	20	-25
2	0	8
3	18	-13
4	0	-0
5	16	-18
6	14	11
K,L=	12,	0
0	82	73
1	78	78
2	14	-13
3	55	-57
4	19	-19
5	17	12
K,L=	13,	0
1	42	37
2	0	-7
3	0	-4
4	0	3
5	0	4
K,L=	14,	0
0	13	10
1	17	-16
2	27	-27
3	17	-14
4	0	0
5	14	15
K,L=	15,	0
1	14	16
2	0	5
3	0	-9
4	8	-6
K,L=	16,	0
0	13	-8
1	0	-5
2	27	18
K,L=	0,	1
0	53	68
1	490	-473
2	0	-23
3	167	173
4	0	1
5	0	11
6	13	10
7	18	22
8	32	-27
-1	192	-219
-2	242	250
-3	126	121
-4	24	-24
-5	132	-140
-6	24	16
-7	34	40
-8	52	-45
K,L=	1,	1
0	165	-250
1	687	-697
2	28	-26
3	26	-25
4	124	136
5	35	47
6	16	15
7	21	-30
8	0	-4
-1	147	151
-2	177	161
-3	152	136
-4	18	1
-5	19	15
-6	49	-60
-7	56	58
-8	0	6
-9	19	17
K,L=	2,	1
0	147	-137
1	153	134
2	65	71
3	38	41
4	26	-26
5	55	-69
6	0	3
7	13	-15
8	0	9
-1	140	127
-2	35	-42
-3	123	113
-4	54	-55
-5	0	-11
-6	15	14
-7	0	17
-8	29	29
K,L=	3,	1
0	27	27
1	109	-99
2	17	4
3	152	156
4	0	9
5	20	22
6	37	-47
7	25	-34
8	0	5
-1	399	374
-2	91	90
-3	148	-150
-4	32	-48
-5	73	-82
-6	0	7
-7	16	-13
-8	0	-3
K,L=	4,	1
0	16	-12
1	99	101
2	0	8
3	136	-133
4	0	-23
5	31	42
6	0	-0
7	34	39
8	31	27
-1	32	-39
-2	0	7
-3	142	-139
-4	29	32
-5	38	42
-6	43	-39
-7	29	-30
-8	0	11
K,L=	5,	1
0	29	25
1	100	88
2	72	-70
3	59	-59
4	24	-24
5	36	-42
6	0	14
7	43	44
8	0	18
-1	142	-134
-2	134	-127
-3	80	-89
-4	0	-3
-5	140	146
-6	109	117
-7	0	5
-8	21	-35
-9	17	-23
K,L=	6,	1
0	132	130
1	25	-14
2	42	-46
3	17	7
4	57	59
5	34	43
6	23	-27
7	47	-52
8	32	-34
-1	0	-9
-2	66	-64
-3	44	-43
-4	47	47
-5	56	68
-6	16	18
-7	0	-12
-8	16	-22
K,L=	7,	1
0	51	53
1	36	44
2	50	49
3	0	-12
4	40	39
5	0	-7
6	0	-3
7	0	-7
8	17	-16
-1	0	-17
-2	70	65
-3	87	87
-4	48	-50
-5	61	-63
-6	72	-71
-7	0	-15
-8	0	9
-9	14	20
K,L=	8,	1
0	27	32
1	11	-18
2	70	-76
3	0	6
4	0	5
5	0	-8
6	58	57
7	0	2
-1	45	41
-2	77	-83
-3	26	31
-4	13	-11
-5	23	-23
-6	0	3
-7	0	-14
-8	0	-3
K,L=	9,	1
0	97	-105
1	49	-54
2	20	-21
3	0	8
4	28	-31
5	40	44
6	0	13
7	0	-11
-1	25	-25
-2	0	4
-3	39	53
-4	86	88
-5	35	-47
-6	0	-18
-7	0	12
-8	27	32
K,L=	10,	1
0	0	-0
1	23	22
2	55	57
3	0	0
4	27	-32
5	18	-20
6	20	-19
7	14	18
-1	21	-22
-2	46	47
-3	16	-18
-4	0	9
-5	0	-7
-6	0	-1
-7	21	22
K,L=	11,	1
0	64	75
1	82	81
2	59	73
3	18	-23
4	25	-33
5	26	-27
-1	0	-1
-2	55	-64
-3	37	-42
-4	0	-8
-5	32	28
-6	0	-8
K,L=	12,	1
0	64	-73
1	0	-15
2	0	10
3	17	-0
4	0	14
-1	0	5
-2	32	33
-3	0	13
-4	18	-22
-5	0	-1
-6	0	-8
K,L=	13,	1
0	21	-23
1	29	-24
2	53	-49
3	0	-1
4	17	16
-1	15	-15
-2	15	17
-3	0	5
-4	0	0
-5	19	19
-6	21	21
K,L=	14,	1
0	12	8
1	0	-3
2	0	5
3	0	12
-1	0	0
-2	0	9
-3	0	10
-4	0	-5
K,L=	15,	1
0	0	4
1	16	-15
2	0	-4
3	21	20
-1	33	29
-2	38	31
-3	0	2
-4	17	-24
K,L=	16,	1
0	18	15
-1	0	-6
-2	15	-17
K,L=	0,	2
0	145	177
1	242	-213
2	231	-235
3	14	-6
4	20	-17
5	52	68
6	15	22
7	0	5
-1	48	52
-2	49	57
-3	20	-7
-4	64	72
-5	50	-60
-6	32	39
-7	29	32
-8	0	12
-9	27	27
K,L=	1,	2
0	57	44
1	19	11
2	254	262
3	0	9
4	19	-21
5	25	-35
6	15	-25
7	0	-9
-1	114	-116
-2	89	-74
-3	24	1
-4	49	60
-5	29	36
-6	52	-58
-7	47	46
-8	0	-9
-9	0	5
K,L=	2,	2
0	41	50
1	125	114
2	72	76
3	11	4
4	28	27
5	19	-26
6	0	3
7	18	-17
-1	24	26
-2	171	-161
-3	15	-13
-4	37	-37
-5	31	37
-6	31	-38
-7	29	-34
-8	0	-11
-9	0	-1
K,L=	3,	2
0	101	-116
1	40	36
2	14	19
3	25	-23
4	68	-76
5	15	11
6	15	20
7	0	8
-1	39	-30
-2	79	-67
-3	39	46
-4	92	97
-5	35	-37
-6	29	-38
-7	0	-13
-8	32	30
-9	0	-3
K,L=	4,	2
0	156	-148
1	29	22
2	47	40
3	31	-31
4	23	-23
5	0	-5
6	15	-22
7	14	20
-1	120	-113
-2	60	60
-3	0	3
-4	80	90
-5	87	86
-6	30	28
-7	15	-21
-8	0	-14
-9	23	-17
K,L=	5,	2
0	47	52
1	42	46
2	59	-55
3	0	-2
4	47	49
5	22	27
6	12	10
7	12	-15
-1	0	-7
-2	58	42
-3	29	22
-4	26	-30
-5	0	-15
-6	0	5
-7	0	-8
-8	0	7
K,L=	6,	2
0	26	26
1	26	-24
2	0	7
3	33	37
4	0	6
5	0	6
6	0	-0
7	0	-2
-1	77	80
-2	118	115
-3	12	-13
-4	118	-135
-5	111	-128
-6	13	-17
-7	42	48
-8	25	29
K,L=	7,	2
0	21	23
1	34	-37
2	0	-14
3	20	-22
4	0	5
5	25	-25
6	0	-7
7	18	20
-1	22	-26
-2	0	1
-3	0	-1
-4	28	-32
-5	24	23
-6	0	9
-7	0	6
-8	16	-16
K,L=	8,	2
0	33	-30
1	57	-62
2	23	-28
3	0	6
4	0	-1
5	16	-17
6	16	21
-1	0	6
-2	29	-26
-3	73	77
-4	24	15
-5	0	7
-6	16	24
-7	18	21
K,L=	9,	2
0	20	-22
1	0	9
2	30	34
3	48	49
4	0	-9
5	0	-4
6	19	-17
-1	55	56
-2	15	-21
-3	34	-37
-4	17	21
-5	0	1
-6	13	23
-7	0	-4
K,L=	10,	2
0	25	26
1	61	66
2	39	46
3	0	12
4	0	-11
5	0	-1
6	14	-16
-1	48	-49
-2	36	-39
-3	50	-51
-4	40	45
-5	14	16
-6	16	-18
-7	31	-33
K,L=	11,	2
0	0	2
1	52	-55
2	29	-30
3	25	-29
4	0	7
5	16	19
-1	22	27
-2	27	29
-3	0	-11
-4	0	-16
-5	0	2
K,L=	12,	2
0	0	-11
1	18	-13
2	47	-37
3	41	-40
-1	29	23
-2	18	13
-3	0	5
-4	0	-1
-5	29	27
K,L=	13,	2
0	0	6
1	39	34
-1	24	-18
-2	0	-1
-3	0	10
-4	0	-9
K,L=	14,	2
0	19	22
-1	12	12
-2	0	-1
-3	0	-13
-4	19	-21
K,L=	15,	2
-1	20	-25
K,L=	0,	3
0	51	-56
1	21	-22
2	70	64
3	135	154
4	0	0
5	0	-7
6	23	-28
-1	75	-75
-2	0	6
-3	27	29
-4	48	56
-5	77	-77
-6	31	25
-7	0	1
-8	14	-6
K,L=	1,	3
0	0	13
1	50	-30
2	94	94
3	21	17
4	0	1
5	0	4
6	0	-16
-1	49	-40
-2	12	-7
-3	56	-52
-4	20	17
-5	0	-0
-6	63	-58
-7	0	-6
-8	27	-24
K,L=	2,	3
0	0	1
1	33	-37
2	26	-23
3	61	-65
4	0	-11
5	0	-16
6	0	18
-1	54	41
-2	17	12
-3	47	38
-4	44	-42
-5	0	15
-6	0	-14
-7	30	22
-8	0	0
K,L=	3,	3
0	57	-52
1	38	-34
2	20	-22
3	0	-5
4	0	-9
5	0	5
6	0	2
-1	89	73
-2	0	5
-3	0	11
-4	48	37
-5	42	41
-6	24	21
-7	0	-13
-8	15	-8
K,L=	4,	3
0	38	33
1	70	72
2	0	-2
3	26	-26
4	19	16
5	36	32
6	0	2
-1	22	12
-2	0	-0
-3	82	-80
-4	24	-22
-5	20	17
-6	0	12
-7	16	-9
-8	14	12
K,L=	5,	3
0	69	63
1	30	30
2	28	-25
3	0	6
4	0	17
5	0	-4
6	0	-1
-1	28	24
-2	0	-1
-3	73	-75
-4	107	-101
-5	34	-32
-6	43	41
-7	27	24
-8	16	10
K,L=	6,	3
0	16	-19
1	16	-20
2	0	-17
3	0	7
4	0	-11
5	0	-12
6	14	-14
-1	41	-34
-2	0	-2
-3	26	30
-4	61	55
-5	16	13
-6	0	-11
-7	28	-26
K,L=	7,	3
0	16	-12
1	22	-25
2	0	-6
3	0	-8
4	0	1
-1	56	-51
-2	28	24
-3	80	71
-4	48	47
-5	18	20
-6	0	-13
K,L=	8,	3
0	24	22
1	0	-6
2	19	24
3	22	25
4	16	16
-1	0	8
-2	49	-45
-3	0	13
-4	0	-7
-5	0	0
-6	0	-9
K,L=	9,	3
0	34	-30
1	40	31
2	43	37
3	14	14
4	0	-11
-1	0	-3
-2	47	-37
-3	0	2
-4	30	18
-5	28	-29
-6	33	-30
K,L=	10,	3
0	0	10
1	0	-1
2	40	-35
3	37	-32
4	20	-22
-1	25	25
-2	40	27
-3	31	-30
-4	0	-5
-5	0	-9
K,L=	11,	3
0	0	13
1	0	-16
2	0	-11
3	24	-21
-1	0	11
-2	22	20
-3	15	-9
-4	0	4
-5	16	13
K,L=	12,	3
0	31	-25
1	14	10
2	31	29
-1	20	-16
-2	0	7
-3	0	5
-4	15	-14

from each carbon atom in the ring, with an isotropic temperature factor of 3.5 Å.^{2} After five cycles of the refinement, the decreasing rate of the R factor seemed to slow down and no significant shifts in the parameters were observed. The final R factor reached 0.107 for the observed reflections. The atomic scattering factors for carbon and nitrogen given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry and Veenendaal,11) and for hydrogen given by McWeeny,12) were used

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11) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

12) R. McWeeny, ibid., **4**, 513 (1951).

Table II. Final atomic coordinates and temperature factors
The anisotropic temperature factors are expressed in the form of
$\exp\text{-}(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.16973	0.15379	0.15405	0.018504	0.006258	0.058048	−0.000558	0.015398	0.000036
C(2)	0.31773	0.13101	0.03132	0.023291	0.007359	0.076423	0.005206	0.008958	−0.006962
C(3)	0.44187	0.20011	−0.08203	0.018138	0.011003	0.067218	0.003689	0.022888	−0.005383
C(4)	0.09801	0.25000	0.22205	0.018590	0.005645	0.027213	0	0.006040	0
C(5)	−0.06160	0.25000	0.35357	0.020446	0.005034	0.057056	0	0.011879	0
C(6)	−0.14449	0.15722	0.44395	0.016152	0.006619	0.082259	0.004031	0.021257	−0.002280
N(1)	−0.20917	0.08564	0.51663	0.023228	0.006313	0.131942	−0.000560	0.046332	0.007021

Atom	x	y	z	B(Å^2)
H(1)	0.1153	0.0917	0.2180	2.97
H(2)	0.3355	0.0574	0.0294	4.72
H(3)	0.5398	0.1701	−0.1674	3.35

Table III. Estimated standard deviations ($\sigma(x)$,$\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
C(1)	0.0061	0.0066	0.0061	0.001286	0.000457	0.005195	0.001338	0.003935	0.002637
C(2)	0.0071	0.0074	0.0070	0.001516	0.000531	0.005990	0.001532	0.004656	0.003063
C(3)	0.0061	0.0075	0.0064	0.001388	0.000676	0.005924	0.001473	0.004333	0.003070
C(4)	0.0087	0	0.0080	0.001780	0.000587	0.006256	0	0.005013	0
C(5)	0.0092	0	0.0089	0.002017	0.000582	0.007830	0	0.006022	0
C(6)	0.0062	0.0069	0.0067	0.001179	0.000475	0.005949	0.001332	0.004128	0.002884
N(1)	0.0058	0.0059	0.0066	0.001329	0.000419	0.006627	0.001312	0.004744	0.002931

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
H(1)	0.055	0.063	0.060	1.55
H(2)	0.063	0.069	0.066	1.86
H(3)	0.057	0.060	0.058	1.63

throughout this structure determination. The observed and calculated structure factors are listed in Table I. The final atomic coordinates and the temperature factors are given in Table II, and their standard deviations, in Table III. The final three-dimensional electron-density distribution, calculated with signs based on these atomic coordinates, is shown in Fig. 5.

The computations were done on a NEAC 2101 computer in the Institute, with programs written by Takano and Nishi, and on an IBM 7090 computer through "UNICON" project, with programs written by one of the present authors (T. A.).

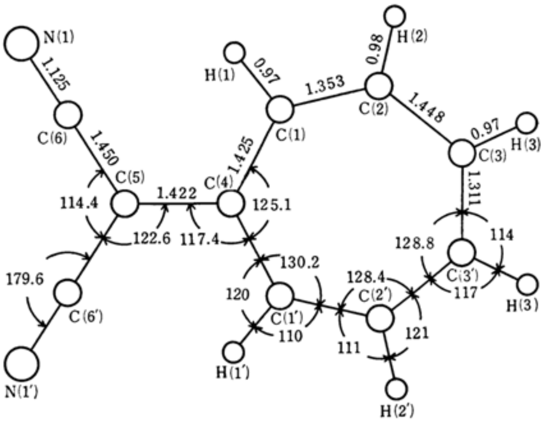

Fig. 6. Bond length (Å) and angles (degrees), without libration corrections.

Discussion

Molecular Geometry.—The intramolecular bond lengths and angles are illustrated in Fig. 6 and are listed in Table IV.

All the bond distances in the dicyanomethylene group are nearly equal to those of the corresponding bonds in 7, 7, 8, 8-tetracyanoquinodimethane[13] (TCNQ) (C≡N = 1.140 Å and C–C = 1.441 Å). They slightly differ from those in pyridinium dicyanomethylide[14] (C≡N = 1.13 Å and C–C = 1.41Å), and TCNQ in a 1 : 1 complex of TCNQ and *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD)[15] (C≡N = 1.160 Å and C–C = 1.412 Å). On the other hand, the length between C(4) and C(5), 1.422 Å, is significantly longer than that of TCNQ, and slightly longer than that of TCNQ in a 1 : 1 complex with TMPD. A comparison of these values with the normal C–C bond lengths seems to suggest a considerable contribution of

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13) R. E. Long, R. A. Sparks and K. N. Trueblood, ibid., **18**, 932 (1965).

14) C. Bugg and R. L. Sass, ibid., **18**, 591 (1965).

15) A. W. Hanson, ibid., **19**, 610 (1965).

TABLE IV. BOND LENGTHS AND ANGLES WITH THEIR e.s.d.'s

Numbers in parentheses are after corrections for libration.
The e.s.d.'s do not include estimated error in libration corrections.

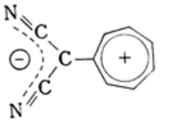
	Distance (Å)		e.s.d.		Angle (deg.)		e.s.d.
C(4)-C(1)	1.425	(1.432)	0.011	C(1)-C(4)-C(1′)	125.1	(125.1)	0.7
C(1)-C(2)	1.353	(1.357)	0.010	C(4)-C(1)-C(2)	130.2	(130.1)	0.7
C(2)-C(3)	1.448	(1.450)	0.011	C(1)-C(2)-C(3)	128.4	(128.3)	0.7
C(3)-C(3′)	1.311	(1.314)	0.015	C(2)-C(3)-C(3′)	128.8	(129.0)	0.7
C(4)-C(5)	1.422	(1.426)	0.013	C(1)-C(4)-C(5)	117.4	(117.4)	0.7
C(5)-C(6)	1.450	(1.454)	0.012	C(4)-C(5)-C(6)	122.6	(122.6)	0.7
C(6)-N(1)	1.125	(1.128)	0.010	C(6)-C(5)-C(6′)	114.4	(114.5)	0.7
C(1)-H(1)	0.97		0.07	C(5)-C(6)-N(1)	179.6	(179.6)	0.7
C(2)-H(2)	0.98		0.07	H(1)-C(1)-C(4)	120		4
C(3)-H(3)	0.97		0.06	H(1)-C(1)-C(2)	110		4
				H(2)-C(2)-C(1)	111		4
				H(2)-C(2)-C(3)	121		4
				H(3)-C(3)-C(2)	117		4
				H(3)-C(3)-C(3′)	114		4

TABLE V. COMPARISON OF BOND LENGTH IN THE LINEAR AND RING CONJUGATED COMPOUNDS

Compound	Average bond lengths			
	C-C	C=C	Mean	Ref.
15, 15′-Dehydro-β-carotene	1.456Å*	1.345Å*	1.401Å*	21
Vitamine-A acid	1.452*	1.361*	1.407*	22
β-Ionyliden crotonic acid	1.466*	1.343*	1.405*	23
7, 7, 8, 8-Tetracyanoquinodimethane	1.448	1.346	1.397	13
p-Benzoquinone	1.477	1.322	1.400	24
Cyclooctatetraenecarboxylic acid	1.470	1.322	1.396	25
Dimethylfulvene	1.438	1.346	1.392	18
1, 2, 3, 4-Tetrachlorobenzo[g]sesquifulvalene	1.45	1.37	1.41	19
1, 2, 3-Tribromo-6-(*o*-methoxyphenyl)fulvene	1.48**	1.31**	1.40**	20
8, 8-Dicyanoheptafulvene	1.437	1.339	1.388	

* These values were obtained from the trans-chain parts.
** These values were obtained from the five-membered ring.

the following dipolar resonance form to the structure:



Thus, the present analysis supports the idea that this dipolar structure must be responsible for the stability of the molecule.[1-3,16,17]

The bond alternation, as suggested by its Kekule formula, is observed in the seven-membered ring. Similar bond alternation has been reported in other non-benzenoid aromatic compounds, dimethylfulvene,[18] 1, 2, 3, 4-tetrachlorobenzo[g]sesquifulvalene,[19] and 1, 2, 3-tribromo-6-(*o*-methoxyphenyl)fulvene.[20] To investigate the extent of bond alternation, average single and double bond lengths in the conjugated cyclic molecules were compared with those in molecules with an all-trans conjugated polyene chain (cf. Table V). The average lengths of single bonds and those of double bonds are approximately constant in the various linear polyenes. On the other hand, these values spread out over a wider range in the cyclic molecules. This may occur as a result of intramolecular strain. However, it may be pointed out that the mean values between the average single and double bond lengths show nearly the same value, 1.40 Å, throughout all the compounds given in Table V.

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16) D. J. Bertelli, C. Golino and D. L. Dreyer, *J. Am. Chem. Soc.*, **86**, 3329 (1964).

17) M. Yamakawa, H. Watanabe, T. Mukai, T. Nozoe and M. Kubo, ibid., **82**, 5665 (1960).

18) N. Norman and B. Post, *Acta Cryst.*, **14**, 503 (1961).

19) Y. Nishi, Y. Sasada, T. Ashida and M. Kakudo, This Bulletin, **39**, 818 (1966).

20) Y. Kato, Y. Sasada and M. Kakudo, ibid., **38**, 1761 (1965).

21) W. G. Sly, *Acta Cryst.*, **17**, 511 (1964).

22) C. H. Stam and C. H. MacGillavry, ibid., **16**, 62 (1963).

23) E. L. Eichhorn and C. H. MacGillavry, ibid., **12**, 872 (1959).

24) J. Trotter, ibid., **13**, 86 (1960).

25) D. P. Shoemaker, H. Kindler, W. G. Sly and R. C. Srivastava, *J. Am. Chem. Soc.*, **87**, 482 (1965).

Even after the rotational corrections, as will be shown later, the C(3)-C(3′) distance is apparently shorter than the C=C distance in ethylene (1.337±0.003 Å).26) Similar situations have been observed elsewhere; a C=C bond distance in *p*-benzoquinone24) is 1.322±0.008 Å, the shortest bond distance in pyrene27) is 1.315±0.020 Å without rotational corrections and 1.320±0.020 Å with the corrections, and the shortest double bond distance in cyclooctatetraenecarboxylic acid25) is 1.310±0.007 Å, while its average double bond distance is 1.322 Å. These values suggest that the C=C distance in ethylene can not be taken as the normal double bond distance in the molecules of this type.28)

Planarity.—The 8, 8-dicyanoheptafulvene molecule is approximately planar, as may be expected from the chemical formula. The detailed analysis of the atomic coordinates shows, however, a slight but significant deviation from this planarity. The equation for the best plane of the molecule, calculated with all twelve heavy atoms equally weighted, is:

$$Z = -0.6048X + 1.2571$$

where $X=ax\sin\beta$, $Y=by$, and $Z=cz+ax\cos\beta$. The large deviations from this plane are 0.059 Å for C(5), −0.040 Å for N(1), and 0.024 Å for C(1). On the other hand, the eight atoms, C(1)-C(5), all lie, within the range of 0.014 Å, on the plane:

$$Z = -0.5834X + 1.2081$$

as is illustrated in Fig. 7. The linear C(5)-C(6)-N(1) unit thus makes an angle of about 2° with this plane. A similar non-planarity has also been reported for the pyridinium dicyanomethylide carbanion14) and TCNQ in a 1 : 1 complex with

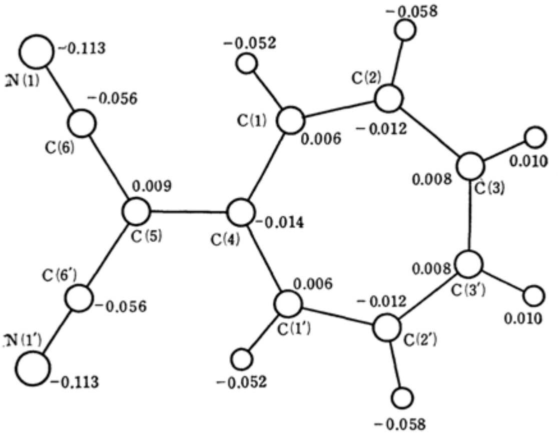

Fig. 7. The deviations (Å) of the atoms from the least-squares plane through atoms C(1)—C(5).

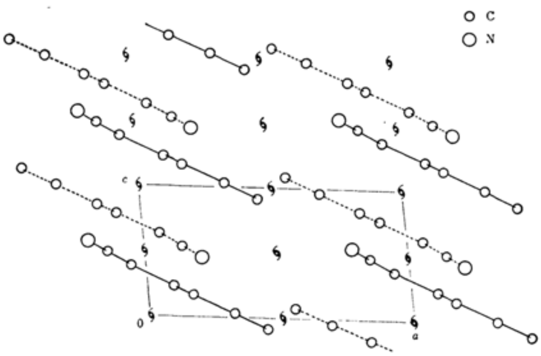

Fig. 8. The crystal structure projected along the b axis. The molecules drawn with brokn lines lie down half-period of the b axis.

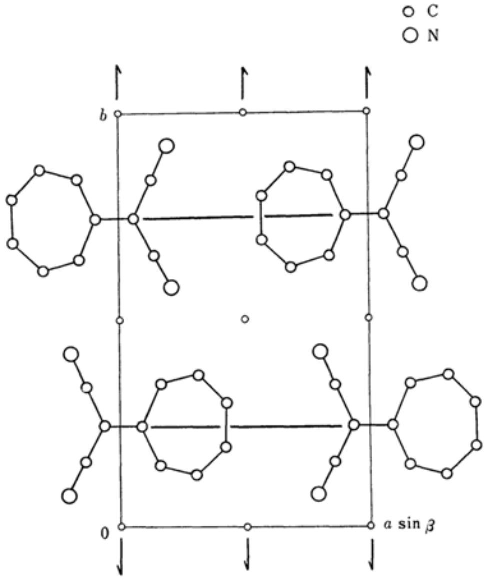

Fig. 9. The crystal structure projected along the c axis.

TABLE VI. SHORT INTERMOLECULAR DISTANCES (Å)

	Atom (molecure 1)	to Atom	in Molecule	Distance
C···C	C(3)	C(6)	4	3.66
C···N	C(1)	N(1′)	2	3.41
	C(2)	N(1′)	2	3.54
	C(2)	N(1′)	3	3.62
	C(3)	N(1)	4	3.70
N···H	H(1)	N(1′)	2	2.62
	H(2)	N(1′)	2	2.88
	H(2)	N(1′)	3	2.94

Molecule				
	1	x	y	z
	2	$-x$	$1/2+y$	$1-z$
	3	$-x$	$1/2+y$	$-z$
	4	$1+x$	y	z

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26) H. C. Allen and E. K. Plyler, ibid., **80**, 2673 (1958).

27) A. Camerman and J. Trotter, *Acta Cryst.*, **18**, 636 (1965).

28) D. W. J. Cruickshank, *Tetrahedron*, **17**, 155 (1962).

TMPD[15]. In TCNQ,[13] however, the molecule is planar within the limit of errors. It may be anticipated that, because of the dipolar resonance structure, the electronic state of the C(5) significantly deviates from the sp^2 hybridization.

Crystal Structure.—The packing diagrams of the crystal of 8, 8-dicyanoheptafulvene viewed along the b and c axes are shown in Figs. 8 and 9 respectively. Short intermolecular distances are listed in Table VI. There are no abnormal intermolecular approaches displayed in the crystal. This compound has the high dipole moment of 7.49 D (in dioxane at 25°C).[17] The arrangement of the molecules appears to be favorable enough to compensate for this high dipole moment.

The molecule lies nearly parallel to the (101) plane at an intermolecular spacing of 3.41 Å, which corresponds to the normal van der Waals contact between the benzenoid rings.

Anisotropic Thermal Motion.—The anisotropic thermal parameters, B_{ij}, were transformed to U tensors referred to the molecular axes, 1, 2 and 3, shown in Fig. 10, the origin of the coordinate system lay at the center of gravity of the molecule. The direction cosines of the molecular axes referred to the orthogonal axes (a*, b, c) are:

TABLE VII. OBSERVED AND CALCULATED U_{ij}, the latter being evaluated with T and ω in Table VIII
(Values in 10^{-2}Å^2)

Atom	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
C(1)	4.38	4.64	5.47	5.45	5.94	6.09	−0.13	0.34	1.21	0.98	−0.07	0.14
C(2)	6.26	4.81	6.44	6.17	6.95	8.25	1.62	−0.11	1.02	0.92	−0.09	0.18
C(3)	3.97	4.41	9.62	7.33	6.95	7.21	1.18	0.11	1.15	0.99	−0.11	0.24
C(4)	4.43	4.33	4.94	5.34	3.51	3.80	0	0.52	1.89	1.04	0	0.06
C(5)	5.04	4.33	4.40	5.70	5.80	4.31	0	0.52	1.38	1.01	0	0.09
C(6)	3.90	4.62	5.79	6.23	7.55	7.06	1.06	1.03	0.31	1.02	0.28	0.06
N(1)	4.82	5.25	5.52	6.83	12.74	12.14	−0.58	1.69	0.60	1.01	0.72	−0.12

TABLE VIII. VALUES OF T_{ij}, ω_{ij} AND THEIR e.s.d.'s, WHEN THE RIGID BODY CONTAINS TWELVE ATOMS
T_{ij} and $\sigma(T_{ij})$ in 10^{-2}Å^2, ω_{ij} and $\sigma(\omega_{ij})$ in deg^2

$$T = \begin{pmatrix} 4.33 & 0.52 & 1.04 \\ & 5.34 & 0.06 \\ & & 3.80 \end{pmatrix} \qquad \omega = \begin{pmatrix} 43.86 & -0.01 & 0.92 \\ & 9.19 & -0.40 \\ & & 6.46 \end{pmatrix}$$

$$\sigma(T) = \begin{pmatrix} 0.27 & 0.25 & 0.28 \\ & 0.35 & 0.36 \\ & & 0.47 \end{pmatrix} \qquad \sigma(\omega) = \begin{pmatrix} 5.61 & 1.34 & 2.40 \\ & 2.50 & 1.79 \\ & & 1.70 \end{pmatrix}$$

TABLE IX. VALUES OF T_{ij}, ω_{ij} AND THEIR e.s.d.'s,
WHEN THE RIGID BODY CONTAINS ONLY SEVEN ATOMS OF THE RING
T_{ij} and $\sigma(T_{ij})$ in 10^{-2}Å^2 ω_{ij} and $\sigma(\omega_{ij})$ in deg^2

$$T = \begin{pmatrix} 4.33 & 0.76 & 1.28 \\ & 5.29 & -0.05 \\ & & 3.94 \end{pmatrix} \qquad \omega = \begin{pmatrix} 29.97 & 0.00 & 1.07 \\ & 8.20 & 0.20 \\ & & 12.15 \end{pmatrix}$$

$$\sigma(T) = \begin{pmatrix} 0.27 & 0.26 & 0.29 \\ & 0.35 & 0.35 \\ & & 0.58 \end{pmatrix} \qquad \sigma(\omega) = \begin{pmatrix} 9.46 & 2.00 & 3.68 \\ & 2.16 & 1.85 \\ & & 1.81 \end{pmatrix}$$

TABLE X. OBSERVED AND CALCULATED U_{ij}, THE LATTER BEING EVALUATED WITH T AND ω IN TABLE IX
(Values in 10^{-2}Å^2)

Atom	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
C(1)	4.38	4.93	5.47	5.49	5.94	5.54	−0.13	0.42	1.21	1.24	−0.07	0.01
C(2)	6.26	5.24	6.44	6.84	6.95	7.23	1.62	−0.42	1.02	1.21	−0.09	0.01
C(3)	3.97	4.49	9.62	9.03	6.95	6.86	1.18	−0.01	1.15	1.27	−0.11	−0.05
C(4)	4.43	4.33	4.94	5.29	3.51	3.95	0	0.76	1.89	1.28	0	−0.05
C(5)	5.04	4.33	4.40	5.96	5.80	4.40	0	0.76	1.38	1.26	0	−0.06
C(6)	3.90	4.88	5.79	6.96	7.55	6.43	1.06	1.72	0.31	1.21	0.28	−0.15
N(1)	4.82	6.06	5.52	8.08	12.74	10.08	−0.58	2.96	0.60	1.12	0.72	−0.37

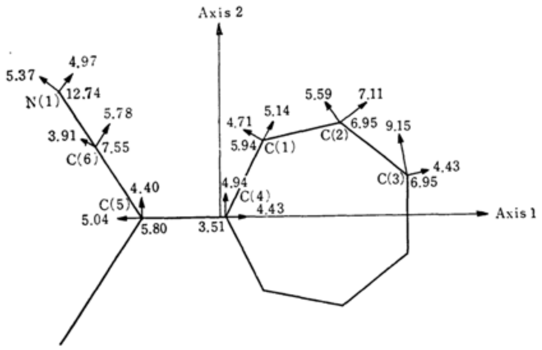

Fig. 10. The values of $\bar{u}^2$ (in unit 10^{-2}Å^2) in the directions radial and tangential to the center, and perpendicular to the molecular plane.

axis 1 : $+0.8717, \quad 0, \quad -0.4900$
axis 2 : $0, \quad 1, \quad 0$
axis 3 : $+0.5175, \quad 0, \quad +0.8557$

The values of the six independent U_{ij}'s for each atom are shown in Table VII in the columns headed 'Obs.' The values of the mean-square oscillation, $\bar{u}^2$, in the directions radial and tangential to the center, and perpendicular to the molecular plane were derived from the U_{ij}'s,29) as is shown in Fig. 10.

If a molecule is rigid-body, the molecular vibration can be expressed in terms of two symmetric tensors, T and ω, the former giving the translational vibrations of the mass center, and the latter the angular oscillations about the axes through the center.30) Given the U tensors for a number of atoms, the T and ω tensors may be determined by the method of least-squares. The resulting T and ω tensors for 8, 8-dicyanoheptafulvene are given in Table VIII. The r. m. s. amplitudes of translational oscillation in the directions of the molecular axes, obtained from the square roots of the diagonal elements of T, are 0.21, 0.23 and 0.19 Å respectively. The corresponding r. m. s. amplitudes of angular oscillation obtained from ω are 6.5°, 3.0° and 2.5°.

While the r. m. s. amplitudes of translational oscillation are nearly equal to each other, those of angular oscillation are different for the three axes. This may be interpreted as indicating a

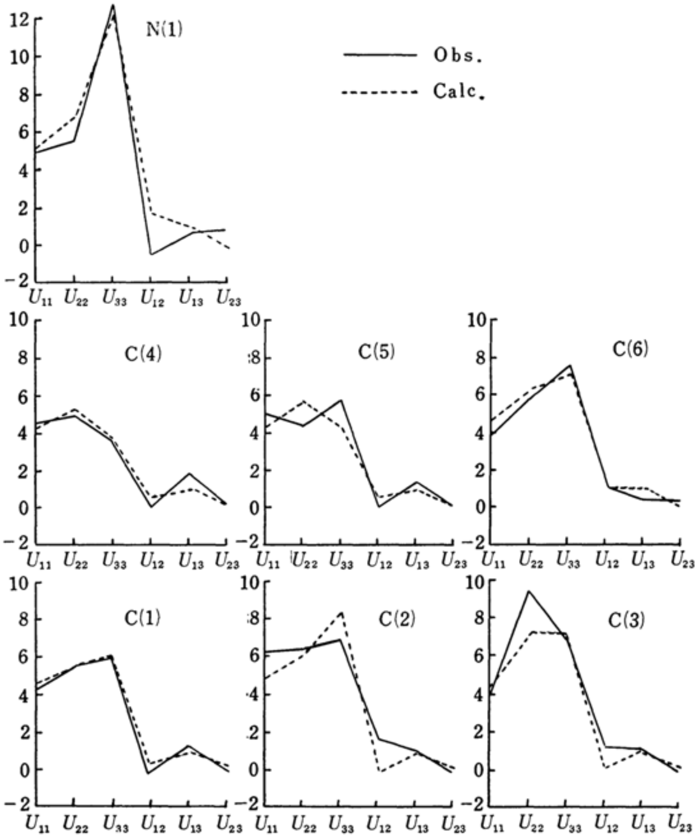

Fig. 11. Comparison between observed and calculated U_{ij}, the latter being evaluated with T and w in Table VIII.

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29) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 747 (1956).

30) D. W. J. Cruickshank, ibid., **9**, 754 (1956).

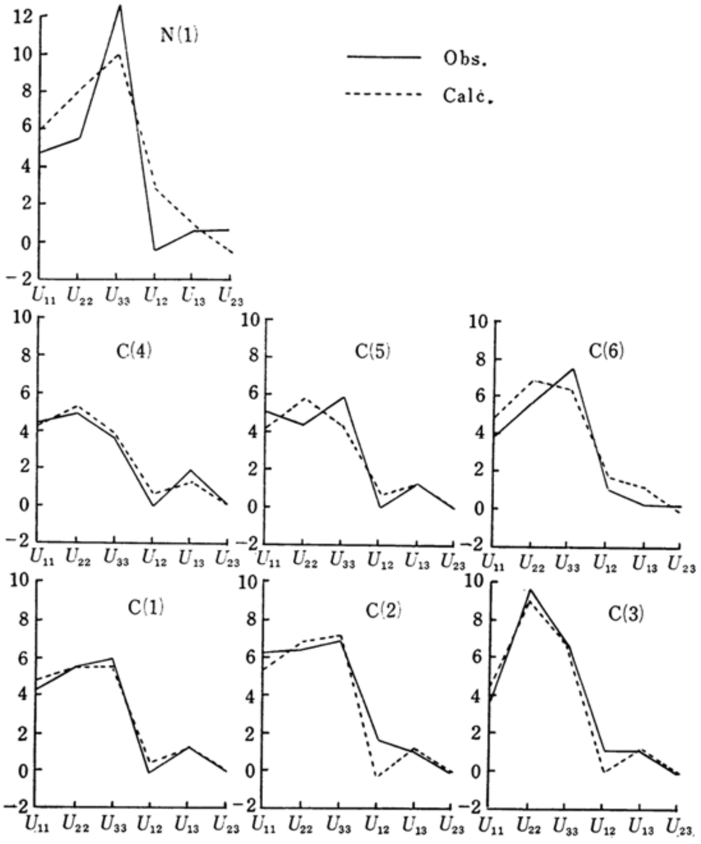

Fig. 12. Comparison between observed and calculated U_{ij}, the latter being evaluated with T and w in Table IX.

difference in the moments of inertia of the molecule around the three axes. The moments of inertia are $I_1=274$, $I_2=698$ and $I_3=972$ g.Å^2/mol. around the 1, 2 and 3 axes respectively. The larger the moment, the smaller the amplitude becomes.

In order to examine the validity of the rigid-body approximation, the U_{ij} values calculated with T and ω are listed in Table VIII in the column headed 'Calcd.' while the observed and calculated U_{ij}'s are compared in Fig. 11. Considerable discrepancies are observed for C(2), C(3) and C(5), which may be due to equal weights for all the atoms in the evaluation. T and ω tensors were, therefore, calculated with only seven atoms in the ring weighted equally, as is shown in Table IX, and the U_{ij}'s were then calculated using these values, as is shown in Table X. The observed and calculated U_{ij}'s are compared in Fig. 12. Good agreements are observed within the seven-membered ring, but in the dicyanomethylene group there are large discrepancies. This may be due to the twisting and scissoring of the exocyclic group.

It is necessary to allow for the angular oscillations causing the atoms to appear too close to the center of the molecule.[31] The radial error in the position of an atom is given by:

$$1/2r\{s^2 / (1 + s^2/q^2) + t^2/(1 + t^2/q^2)\},$$

where s^2 and t^2 are the mean-square amplitudes of the angular oscillation in the molecular plane and in the direction perpendicular to it respectively, where q^2 is the Gaussian peak-width parameter for an atomic peak without the angular oscillations, and where r is the distance from the point of origin. The two mean-square amplitudes, s^2 and t^2, were calculated from ω_{ij}'s by Cruickshank's equation.[30] Using a value of q^2, 0.112 Å^2, the corrected bond distances and angles were calculated to be as shown in parentheses in Table IV. The corrected C(3)-C(3') distance is still shorter than the C=C distance in ethylene, as has been stated above.

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[31] D. W. J. Cruickshank, ibid., **9**, 757 (1956).